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# Comparison of the Properties of ex-DC and -AUC $UO_2$ pellet

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## ABSTRACT

*Properties of the DC and AUC pellets which were supplied to the commercial reactors in korea had been evaluated. Ex-DC $UO_2$ powder showed lower specific surface area than ex-AUC $UO_2$ powder due to its morphology. Since surface area of ex-AUC $UO_2$ powder was large, it had more chance to oxidation. This leaded to raise O/U ratio. Apparent density of granulated ex-DC $UO_2$ powder was similar to ex-AUC $UO_2$ powder. There was no great difference in sintered density between DC and AUC pellet though DC pellet contained more $U_3O_8$ and was sintered at lower temperature than AUC pellet. DC and AUC pellets showed similar grain size and their average size was about 7.5㎛. DC pellet absorbed less hydrogen than AUC pellet.*

## 1. Introduction

There are two commercial methods to produce $UO_2$ powders from $UF_6$[1]; wet and dry conversion process. The wet conversion is a process where the intermediate products are precipitated from aqueous solutions. On the contrary, the dry conversion is a process through gas reactions where $UF_6$ is directly processed to $UO_2$ powder. AUC process is the first developed and commercially used wet conversion method in which ammonium uranyl carbonate(AUC) is precipitated as a intermediate product. In general, $UO_2$ powder produced from AUC conversion has a good flowability so that it can be compacted without a granulation step. Different from the ex-AUC $UO_2$ powder, the particle size of the $UO_2$ powder obtained from DC conversion process is so fine that the granulation process should be included before compaction to make green pellet. Due to the differences of powder characteristics, properties of DC and AUC pellet are quite different. KNFC(Kepco Nuclear Fuel Co.) has manufactured $UO_2$ powder in its AUC conversion facility since 1990. As atomic reactor increases, the demand of $UO_2$ powder is overwhelmed the production capacity of the KNFC. To solve this problem, KNFC had begun to construct a new DC $UO_2$ conversion line. Due to the different powder characteristics and manufacturing processes, it is essentially needed to verify the properties of DC pellet in comparison with AUC pellet.

This work has been undertaken to provide the basic information on ex-DC $UO_2$ powder and pellet as well as to confirm the integrity of the DC pellet by comparing its properties with AUC pellet.

## 2. Experiments

Samples treated in this paper were taken from pellets which were supplied to commercial reactor in korea. All data used were measured as a Quality Assurance activity and the number of samples were determined based on Mil–STD-414[2] and Mil-STD-105D[3] standard. Sintering variables and other conditions are illustrated in Table 1. All the AUC pellet were sintered at 1750$^{o}$C and the sintering temperature of DC pellet was 1730 $^{o}$C. The sintering time and atmosphere were the same as 5hr and $H_2$.

Characteristics of DC powder were examined using virgin powder except apparent density that was measured using granulated powder. Sintered density and resintered density were measured by geometric method. All the other properties of the pellet were obtained from testing based on ASTM Standard.

## 3. Manufacturing Procedures

### 1) $UO_2$ Powder

Fig. 1 shows the overview of manufacturing steps of ex-AUC and ex-DC $UO_2$ powder conversion process.[4] Ex-AUC $UO_2$ powder is free-flowing because the particle corners and edges are rounded off by stirring the solution during an AUC precipitation and its shape nearly unchanged after the later transformation of the coarse AUC particles into $UO_2$ powder.

AUC conversion process proceeds with five different steps as shown in Fig. 1. The first step is the vaporization of $UF_6$. The vaporization of $UF_6$ is carried out with steam and vaporized $UF_6$ is transformed to AUC($(NH_4UO_2(CO_3)_3$) in a precipitator filled with demineralized water adding $UF_6$, $CO_2$ and $NH_3$ through a nozzle system. AUC particles are pumped to a vacuum filter and successively washed with a solution of ammonium-carbonate and methyl alchol. After filtration process, a transformation of AUC to $UO_2$ is performed in a fluidized bed furnace. The last process is the oxidation of $UO_2$ powder.

Unlike the AUC conversion, in the DC process, $UF_6$ is directly converted to $UO_2$

powder without producing intermediate. DC conversion also starts with the vaporization of $UF_6$. The feed material is reacted with steam in the gas phase at rotating kiln to give an active uranyl fluoride($UO_2F_2$) which is converted in ceramic $UO_2$ in a countercurrent flow of $H_2$ and steam. Pyrohydrolysis consists of two chemical reactions, namely, defluorination reaction and $H_2$ reduction reaction. Morphological change of the particles takes place during defluorination in rotating klin. $UO_2$ powder converted from vaporized $UF_6$ is cooled and outlet from rotating klin

2) Pellet

Pelletizing procedures are shown in Fig.2. In the DC process, a pre-compacting of the $UO_2$ powder is additionally performed to increase compactibility of the DC powder comparing to the AUC process. About 0.3% zinc stearate and 0.5% AZB are added in the DC powder as lubricant and pore former, respectively. Owing to the addition of pore former, the fraction of large pore in the DC pellet is higher than in the AUC pellet.

## 4. **Results and Discussion**

1) Powder properties

Ex-AUC $UO_2$ powder has a unique morphology containing many small crystallites (about ~0.1μm) and they lead to increase specific surface area of the ex-AUC $UO_2$ powder(Fig. 3). Fig. 4 shows the specific surface area of ex-AUC and ex-DC $UO_2$ powder. The specific surface area of ex-DC $UO_2$ powder is 2.26 $m^2/g$ and its value is about a half of ex-AUC (5.14$m^2/g$). Since ex-AUC $UO_2$ powder has larger surface area than ex-DC $UO_2$ powder, ex-AUC $UO_2$ powder has a strong tendency to oxidation and it results in higher O/U ratio.(Fig. 5) Apparent density is an important property because it has an effect on compactibility of the powder. Both ex-AUC $UO_2$ powder and ex-DC $UO_2$ powder exceed the lower limit of specification and have similar values between 2.2 and 2.3$g/cm^3$, respectively(Fig.6). Apparent density of the ex-DC $UO_2$ powder was measured after granulation process.

2) Pellet properties

The sintered densities of AUC and DC pellet are shown in Fig. 7. In the specification[5],[6], density of the pellet is regulated in the range of 94%T.D (10.30 $g/cm^3$) and 96.5%T.D.(10.58$g/cm^3$). Sintered density can be controlled by changing the sintering conditions or adding $U_3O_8$ powder and other substances such as pore former.

In the DC pellet, about 15% $U_3O_8$ and 0.5% pore former were added. On the contrary, the AUC pellet included about 7% $U_3O_8$ and 4% grind sludge without pore former. It is well known that the addition of $U_3O_8$ decreases the sintered density of the pellet. The density drop caused by the addition of $U_3O_8$ can be understood from the fact that the theoretical density of $U_3O_8$ is 8.40 g/cm$^3$.

Pore former has the same effect on sintered density as $U_3O_8$ by volatilizing itself during firing. The site which pore former resides becomes pore and it prevents the pellet from densification. Therefore, the size of pore created by volatilizing pore former strongly depends on particle size of pore former. AZB(**AZ**odicar**B**onamide) is currently used as a pore former in KNFC. Its average particle size is about 8μm. Fig. 8 is a ceramograph of DC and AUC pellet. Many large and spherical pores over 10μm can be seen in the DC pellet. The shape of pores in AUC pellet is irregular and their size is fine. It can be anticipated that AUC pellet has higher density than DC pellet from these facts if the sintering conditions are the same. However, DC pellet sintered at 1730°C has a similar density as AUC pellet sintered at 1750°C though more $U_3O_8$ and pore former are added in DC pellet as shown in Fig. 7.

Fig. 9 exhibits sintered density of DC and AUC pellet in which no other substances are added excluding $UO_2$ powder. In spite of the fact that sintering temperature of AUC pellet is higher than that of DC pellet, DC pellet indicates higher density than AUC pellet. Therefore, it can be deduced from the above results that ex-DC $UO_2$ powder is better than ex-AUC $UO_2$ powder in terms of sinterability. The good sinterability of ex-DC $UO_2$ powders can be attributed to their morphology. Ex-DC $UO_2$ powder consists of aggregates of single particles which arrange themselves during the pressing phase to yield a slug with a pore size distribution featuring a single tightly clustered peak grouped around 0.1 μm, promoting good sinterability.

Hydrogen content in the pellet is extremely confined because it is the source of hydride in the cladding tube. $UO_2$ pellet is dried before loading into the rod in order to reduce the amount of hydrogen in the pellet. It has been known that hydrogen content in the pellet is dependent upon open porosity. Hydrogen is absorbed through open porosity. Open porosity is reduced as sintered density increases. In general, DC pellet having about 95% T.D. of sintered density includes 0.3% of open porosity compared to 0.8% of AUC pellet. In order to reduce open porosity, the lowest limit of sintered density of AUC pellet set as 10.42g/cm$^3$ instead of 10.30g/cm$^3$. Fig.10 shows hydrogen content in the pellet. Hydrogen content in DC pellet is lower than in AUC pellet. Resintered density change is shown in Fig 11. All the pellets meet the specification limit. Fig.12 shows grain size of AUC and DC pellet. As expected, there is no significant difference. The average grain size of AUC pellet and DC pellet is 7.5 μm and 7.6μm, respectively.

## 5. **Conclusions**

The properties of AUC and DC pellet which were supplied to commercial reactors have been examined and obtained the following results.

1)Ex-AUC $UO_2$ powder has many crystallites, which lead to higher specific surface area than ex-DC $UO_2$ powder. Because of small surface area, ex-DC $UO_2$ powder has high resistivity to oxidation. Consequently, ex-DC $UO_2$ powder indicates low O/U ratio compared to ex-AUC $UO_2$ powder. After granulation, granulated ex-DC $UO_2$ powder shows higher apparent density than ex-AUC $UO_2$ powder. But the difference is quite small.

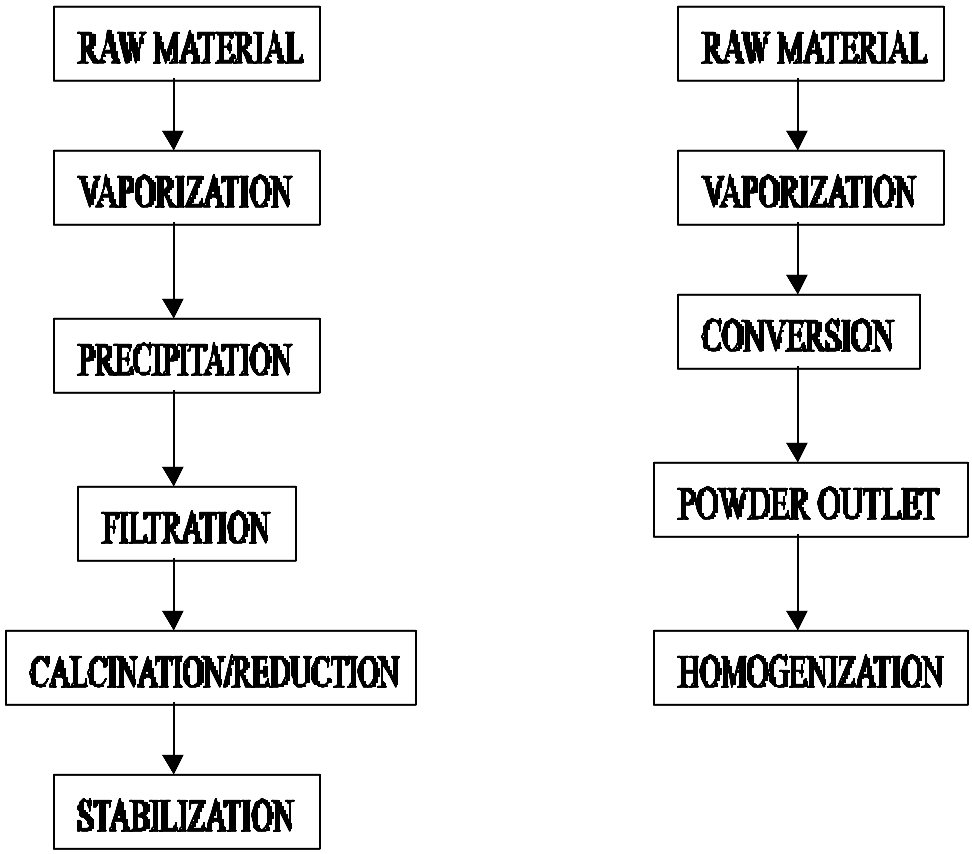
2)DC pellet excluding $U_3O_8$ and pore former has higher density than AUC pellet. Though sintered at lower temperature, DC pellet in which more $U_3O_8$ powder is added has similar sintered density to AUC pellet. The resintered density changes of the pellets are well within the specification limit. DC pellet absorbs less hydrogen than AUC pellet due to small fraction of open porosity in the pellet. Both two pellets have similar grain size.

## 6. References


1) I.S. Chang, M.H. Yoon, Overview of Nuclear Fuel Cycle Engineering, KAERI(1989)
2) Mil-STD-414, Sampling Procedures and Tables for Inspection by Variables for Percent Defective
3) Mil-STD-105D, Sampling Procedures and Tables for Inspection by Attributes
4) S.H. Na, Introduction to Nuclear Fuel Cycle Engineering, KAERI(1994)
5) KNFC Specification, PD31029, Rev.1
6) KNFC Specification PD10001, Rev.0

**Table 1. Adding substances and sintering conditions of DC and AUC pellet**

| | AUC | DC |
|---|---|---|
| Adding Substances | | |
| $U_3O_8$ | 7 – 8 % | 15% |
| Grind Sludge | 3.5 – 4 % | - |
| Zinc Stearate | - | 0.3% |
| Pore former | - | 0.42 – 0.47% |
| Sintering Variables | | |
| **Temperature** | 1750$^{o}$C | 1730$^{o}$C |
| Time | 5.58 – 5.8 hrs | 4 – 4.4 hrs |




(a) (b)

Fig. 1 Schematic diagram of $UO_2$ powder conversion process
(a) AUC process (b) DC process

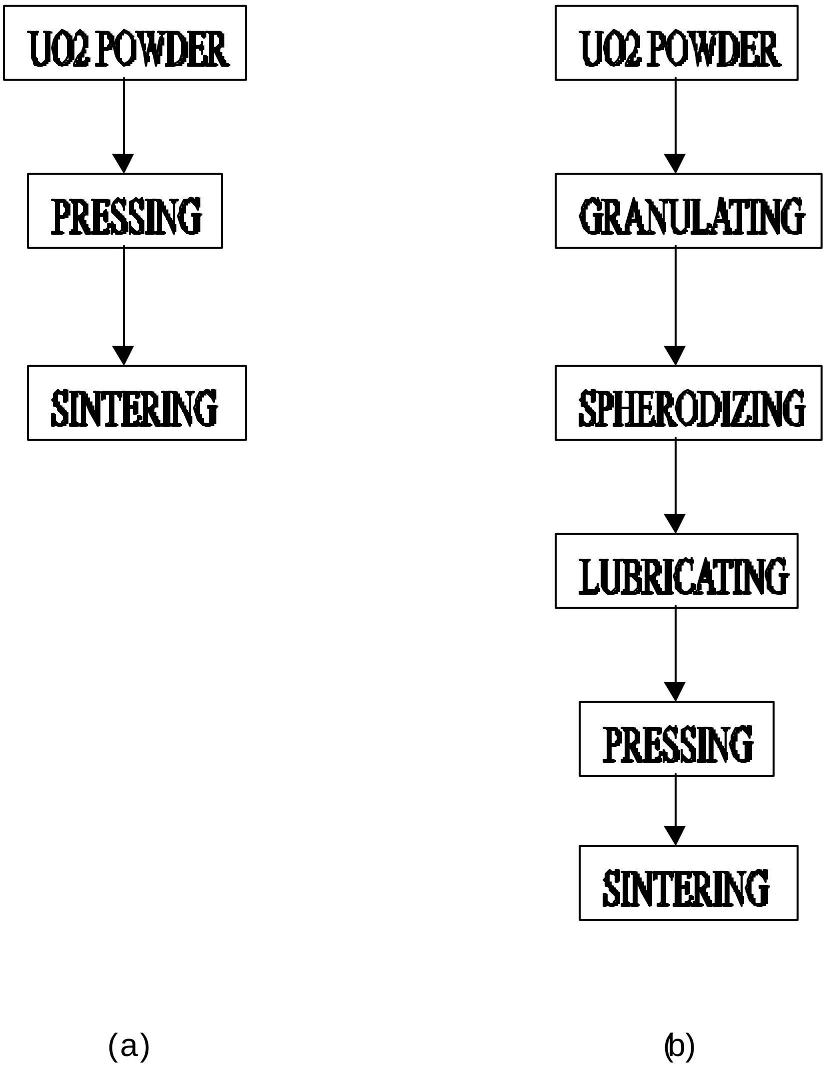



Fig. 2 Schematic diagram of $UO_2$ pelletizing process
(a) AUC process (b) DC process